

Statistical prefactor and nucleation rate near and out of the critical point

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Abstract

The nucleation rate derived in the classical theory contains at least one undetermined parameter, which may be expressed in terms of the Langer first-principles theory. But the uncertainties in the accounting for fluctuation modes, which are either absorbed into the free energy of a critical cluster or not, result in different evaluations of the statistical prefactor and nucleation rate. We get the scaling approximations of the nucleation rate for the vapour condensation both near and out of the critical range. The results obtained deserve the experimental verification to resolve the theoretical uncertainty.

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The homogeneous nucleation occurred in metastable states has been area of much theoretical and experimental activity since time of Maxwell and Van der Waals. The classical nucleation theory was worked out about 60 years ago mainly by Volmer, Becker and Döring, Zeldovich, and Frenkel [1–4]. Under the treatment of relaxation of the initially homogeneous metastable state as a kinetic process, triggered by the creation of spherical clusters of the new, stable, phase as thermal fluctuations in the metastable phase, the classical theory provides us the fundamental nucleation rate

$$I = I_0 \exp \left(-\frac{\Delta F_c}{k_B T} \right) , \quad (1)$$

where I_0 is a pre-exponential factor, ΔF_c is the minimum work needed to create critically large cluster of radius R_c , k_B is Boltzmann constant, and T is the temperature of the system. The nucleation rate yields the number of viable clusters of the new phase per unit volume passing through the critical region per unit time via the equilibrium number of critical clusters $f_0(R_c)$ given by the theory of thermal fluctuations. Usually [4,5] Eq. (1) is rewritten in the form

$$I = B(R_c) f_0(R_c) Z , \quad (2)$$

containing the size diffusion coefficient $B(R_c)$ and the Zeldovich factor

$$Z = \left(\frac{\gamma}{2\pi k_B T} \right)^{1/2} , \quad \gamma = - \left(\frac{\partial^2 \Delta F(R)}{\partial R^2} \right)_{R=R_c} . \quad (3)$$

This is the principal result of the classical theory. According to the thermodynamic theory of fluctuations the multiplicities of clusters of various sizes obeys the Boltzmann (or rather Gibbs) distribution

$$f_0(R) = C_0 \exp \left(-\frac{\Delta F(R)}{k_B T} \right) , \quad (4)$$

and the coefficient C_0 is not determined in the classical theory. To find out the diffusion coefficient $B(R_c) \propto 1/(R - R_c) (dR/dt)_{R=R_c}$ one has to solve the macroscopic equations considering, for instance, the growth of a cluster due to the diffusion flux through its interface.

The coarse-grained field theoretical approach to the nucleation phenomenon was developed by Langer [6,7], who generalized the earlier works of Landauer and Swanson [8], and Cahn and Hilliard [9]. The prefactor I_0 in the theory of Langer is shown to be a product of the dynamical prefactor κ and the statistical prefactor Ω_0

$$I_0 = \frac{\kappa}{2\pi} \Omega_0 , \quad (5)$$

and both prefactors are determined explicitly in the theory. The dynamical prefactor is related to the growth rate of the critical cluster, and the statistical prefactor is a measure of the phase space volume available for the nucleation. Since the beginning of 70's, the Langer theory has been applied to describe first order phase transition in various systems including the vapor condensation [10,11], nucleation in binary fluids [12], solidification of the melt [13], and hadronization of the quark–gluon plasma [14,15], produced in heavy–ion collisions.

As was shown by the authors recently [16], nucleation rate (5) of the field nucleation theory may be obtained under the certain assumptions in a form identical to that of the classical theory. It means, particularly, that one is able to determine the unknown constant C_0 in terms of the modern theory. However, in the present paper we show that the difficulties in the evaluation of Ω_0 give rise to the uncertainty in the determination of the nucleation rate, which can be clearly verified experimentally.

Our arguments are the following. According to the nucleation theory, both classical and modern, the relaxation of the homogeneous metastable state proceeds via the formation of clusters of the new, stable, state. The free energy density functional $F(\{\eta\})$ of the system has two local minima in the configuration phase space $\{\eta\}$, described by a set of N collective coordinates η_i , corresponding to the states of metastable and stable equilibrium. These wells in the phase space are separated by the potential barrier related to the formation of cluster (or fluctuation) of critical size. The nucleation rate is determined by the finite probability flux from the metastable configuration to the stable one across the vicinity of point with the lowest energy on the potential barrier, the so-called saddle point.

In the harmonic approximation for F the statistical prefactor appeared in Langer theory

reads [17]

$$\Omega_0 = V \left(\frac{2\pi k_B T}{|\lambda_1|} \right)^{1/2} \left[\frac{\det(M'/2\pi k_B T)}{\det(M_0/2\pi k_B T)} \right]^{-1/2}. \quad (6)$$

Here V is the volume of the system, M_0 and M denote the matrix $M_{ij} = \partial^2 \Delta F / \partial \eta_i \partial \eta_j$, evaluated at the metastable minimum $\{\eta_0\}$ and at the saddle point, and λ_1 is the only negative eigenvalue of M , associated with the instability of the critical cluster against expansion or shrinking. The prime in Eq. (6) indicates that the eigenvalue λ_1 is omitted. Then, the translational symmetry is broken because of the presence of critical cluster. These three translational modes with zero eigenvalues give rise to the factor [6] proportional to $(|\lambda_1|)^{-3/2}$, and Eq. (6) is transformed into

$$\Omega_0 = \mathcal{V} \left(\frac{2\pi k_B T}{|\lambda_1|} \right)^{1/2} \prod_{\alpha=5}^N \left(\frac{2\pi k_B T}{\lambda_\alpha^{(S)}} \right)^{1/2} \prod_{\beta=1}^N \left(\frac{\lambda_\beta^{(0)}}{2\pi k_B T} \right)^{1/2}, \quad (7)$$

$$\mathcal{V} = V \left(\frac{8\pi\sigma}{3|\lambda_1|} \right)^{3/2}. \quad (8)$$

From here the uncertainties in the determination of the Ω_0 begin. If the products over β and α are absorbed [7] into the free energy of the metastable state and the saddle point, respectively, then Eq. (8) is reduced to

$$\Omega_0^{(1)} = \mathcal{V} \frac{32\pi^2 (k_B T)^{1/2}}{|\lambda_1|^2} \left(\frac{\sigma}{3} \right)^{3/2}, \quad (9)$$

If, on the other hand, one will pair [10] the eigenvalues $\lambda_\alpha^{(S)}$ and $\lambda_\beta^{(0)}$ so, that the corrections to the free energy difference remain of order R_c^3/V in the limit $V \rightarrow \infty$, there will be four unpaired eigenvalues $\lambda_\beta^{(0)}$'s at the bottom of the spectrum of eigenvalues

$$\lim_{R \rightarrow \infty} \prod_{\beta=1}^4 \left(\lambda_\beta^{(0)} \right)^{1/2} = \left(\frac{1}{2\pi k_B T} \frac{\partial^2 f}{\partial n_g^2} \right)^2, \quad (10)$$

where the second derivative of the Helmholtz free energy f with respect to the local density n_g is inversely proportional to the correlation length ξ squared, $\partial^2 f / \partial n_g^2 \propto \xi^{-2}$. The statistical prefactor in the latter case turns out to be

$$\Omega_0^{(2)} = \mathcal{V} \left(\frac{2}{3\sqrt{3}} \right) \left(\frac{\sigma}{k_B T} \right)^{3/2} \left(\frac{R_c}{\xi} \right)^4. \quad (11)$$

To make a comparison between the nucleation rates calculated with $\Omega_0^{(1)}$ and $\Omega_0^{(2)}$ one should know also the dynamical prefactor κ and the minimum work needed to form the critical cluster. For simplicity, let us consider the process of vapour condensation at the condensation point T , corresponding to a certain pressure p_0 . If the vapour is overcompressed with respect to p_0 , the critical radius is determined by the expression

$$R_c = \frac{2\sigma}{\Delta\mu\Delta n} = \frac{2\sigma v_l}{\Delta\mu} , \quad (12)$$

where v_l is the volume per particle of the liquid phase, Δn is the difference in local number densities, and $\Delta\mu$ is the difference in chemical potentials of the vapour and liquid phase

$$\Delta\mu = \mu_v - \mu_l = k_B T \ln \frac{p}{p_0} . \quad (13)$$

Ratio p/p_0 indicates the degree of supersaturation in the system. We see that in the capillary approximation the critical radius scales near the condensation point as $(\ln \epsilon)^{-1}$. Since for the only negative eigenvalue λ_1 one gets $\lambda_1 = -2\lambda_Z^2 k_B T$ [16], where the similarity number [18] is given by $\lambda_Z = (4\pi\sigma/k_B T)^{1/2} R_c$, the statistical prefactor $\Omega_0^{(1)}$ should increase with the rise of ϵ ,

$$\Omega_0^{(1)} \propto (\ln \epsilon)^4 , \quad (14)$$

while $\Omega_0^{(2)}$ drops inversely proportional to the same rate

$$\Omega_0^{(2)} \propto (\ln \epsilon)^{-4} . \quad (15)$$

For the dynamical prefactor we have [11,12]

$$\kappa = \frac{2\lambda\sigma T v_l^2}{l^2 R_c^3} \propto (\ln \epsilon)^3 . \quad (16)$$

Here λ is the heat conductivity and l is the latent heat. The excess of the free energy due to formation of the critical cluster is simply

$$\frac{\Delta F_c}{k_B T} = \frac{\lambda_Z^2}{3} = \frac{b_0}{(\ln \epsilon)^2} , \quad (17)$$

containing the parameter $b_0 = 16\pi(\sigma/k_B T)^3 v_l^2/3$.

Combining our results we get that the nucleation rate is proportional either to the factor $\alpha_1(\epsilon)$ or to the factor $\alpha_2(\epsilon)$, correspondingly,

$$I^{(1)} = \frac{\kappa}{2\pi} \Omega_0^{(1)} \exp\left(-\frac{\Delta F_c}{k_B T}\right) \propto (\ln \epsilon)^7 \exp\left(-\frac{b_0}{(\ln \epsilon)^2}\right) \equiv \alpha_1(\epsilon) , \quad (18)$$

$$I^{(2)} = \frac{\kappa}{2\pi} \Omega_0^{(2)} \exp\left(-\frac{\Delta F_c}{k_B T}\right) \propto (\ln \epsilon)^{-1} \exp\left(-\frac{b_0}{(\ln \epsilon)^2}\right) \equiv \alpha_2(\epsilon) . \quad (19)$$

Figure 1 depicts the evolution of both α_1 and α_2 with the changing of the degree of supersaturation ϵ for different values of the parameter b_0 . The rapid falloff of the exponential at $\epsilon \rightarrow 1$ dominates the increase of the statistical prefactor $\Omega_0^{(2)}$, and although

$$\lim_{\epsilon \rightarrow 1} \Omega_0^{(1)} = 0 \quad \text{and} \quad \lim_{\epsilon \rightarrow 1} \Omega_0^{(2)} = \infty , \quad (20)$$

the nucleation rate in both cases drops to zero near the condensation point and rises up when the vapour is overcompressed. But the slopes of $dI/d\epsilon$ are different, and this disagreement in theoretical predictions may be verified experimentally. Note that in the region near the value $\epsilon = e = 2.7318\dots$ the slopes are similar. Therefore, the measurements should be carried out either with relatively weak supersaturations, or with the strong ones, say $\epsilon \approx 5$, which is still below the limit of supersaturation [19] obtained in the experiments on homogeneous nucleation in vapour.

Near the critical point we should take into account the power-law approximations for the thermodynamic quantities appeared in the nucleation rates, and the critical indices come into play. These quantities are listed in Table I as functions of the standard dimensionless variable $\theta = 1 - T/T_c$ for the vapour side of the coexistence curve at $T < T_c$.

From Table I it follows that the difference of the pressures Δp inside and outside the droplet is $\Delta p = \Delta n \Delta \mu \propto \theta^{\beta+\gamma}$ and, consequently, $R_c \propto \theta^{2\nu-\beta-\gamma}$ and $\lambda_Z \propto \theta^{3\nu-\beta-\gamma}$.

It is worth noting that $\lambda_Z \rightarrow 0$ as $\theta^{3/8}$ at $T \rightarrow T_c$. Therefore the formulae (9) and (11) cannot be applied to calculate the nucleation rate [20] because the criterion $k_B T/|\lambda_1| \ll 1$ of the steepest descent method is not fulfilled. To estimate the difference between the two approaches, however, one may apply the droplet model of Fisher [21] instead of performing

of numerical evaluation of the integrals. In the Fisher model the only negative eigenvalue λ_1 is [20]

$$\lambda_1 = k_B T (9\tau + 2\lambda_Z^2) , \quad (21)$$

where $\tau \approx 2.2$ is the critical exponent. Although the critical radius R_c^F determined in the Fisher model does not coincide with that of the capillary approach, it has the same scaling behaviour, $R_c^F \propto \theta^{2\nu-\gamma-\beta}$, in the proximity of the critical point. The free energy of a critical droplet is given by

$$\frac{\Delta F_c^F}{k_B T} = \tau \left(1 - 3 \ln \frac{R_c^F}{r_{min}} \right) - \frac{\lambda_Z^2}{3} , \quad (22)$$

where r_{min} is the radius of a single molecule. This yields for the exponential factor at $T \rightarrow T_c$

$$\exp \left(\frac{\Delta F_c^F}{k_B T} \right) \propto \theta^{3\tau(\gamma+\beta-2\nu)} . \quad (23)$$

Substituting Eq. (21) in Eq. (9) we find that near the critical point

$$\Omega_0^{(1)} \propto \theta^{3\nu} , \quad (24)$$

and, consequently,

$$I^{(1)} = \text{const}_1 \times \theta^{2\gamma+3\tau(\gamma+\beta-2\nu)} \approx \text{const}_1 \times \theta^{3.6} . \quad (25)$$

Similar estimations of the statistical prefactor $\Omega_0^{(2)}$ lead to the following parametrizations

$$\Omega_0^{(2)} \propto \theta^{15\nu-4\gamma-4\beta} , \quad (26)$$

and

$$I^{(2)} = \text{const}_2 \times \theta^{12\nu-2\gamma-4\beta+3\tau(\gamma+\beta-2\nu)} \approx \text{const}_2 \times \theta^{5.1} . \quad (27)$$

We see again that the resulting power-law approximation of the nucleation rate $I^{(2)}$ as a function of θ deviates clearly from that obtained for $I^{(1)}$.

In conclusion, we study the effect of absorption of the fluctuation corrections to the excess free energy of a cluster into the cluster activation energy. To compare different predictions

made by the Langer coarse-grained field theory of nucleation for the statistical prefactor Ω_0 we choose the liquid–gas phase transition near and out of the critical point. It is shown that although the statistical prefactor drops to zero in the first case and goes to infinity in the other one near the condensation point far from the critical region, the qualitative behaviours of the nucleation rates are similar. However, the power-law parametrizations of the nucleation rate as a function of supersaturation are different. The disagreement between the predictions is especially noticeable in the region of very weak or, in contrast, strong supersaturations.

The scaling behaviour of the statistical prefactor and total nucleation rate is studied also near the critical point in the Fisher droplet model. The qualitative dependences of Ω_0 and I on the scaling parameter $\theta = 1 - T/T_c$ are similar in both approaches, while the analytic parametrizations are different again: $\theta^{3.6}$ vs $\theta^{5.1}$. The experiments on homogeneous condensation of a vapour may certainly resolve this theoretical ambiguity.

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FIGURES

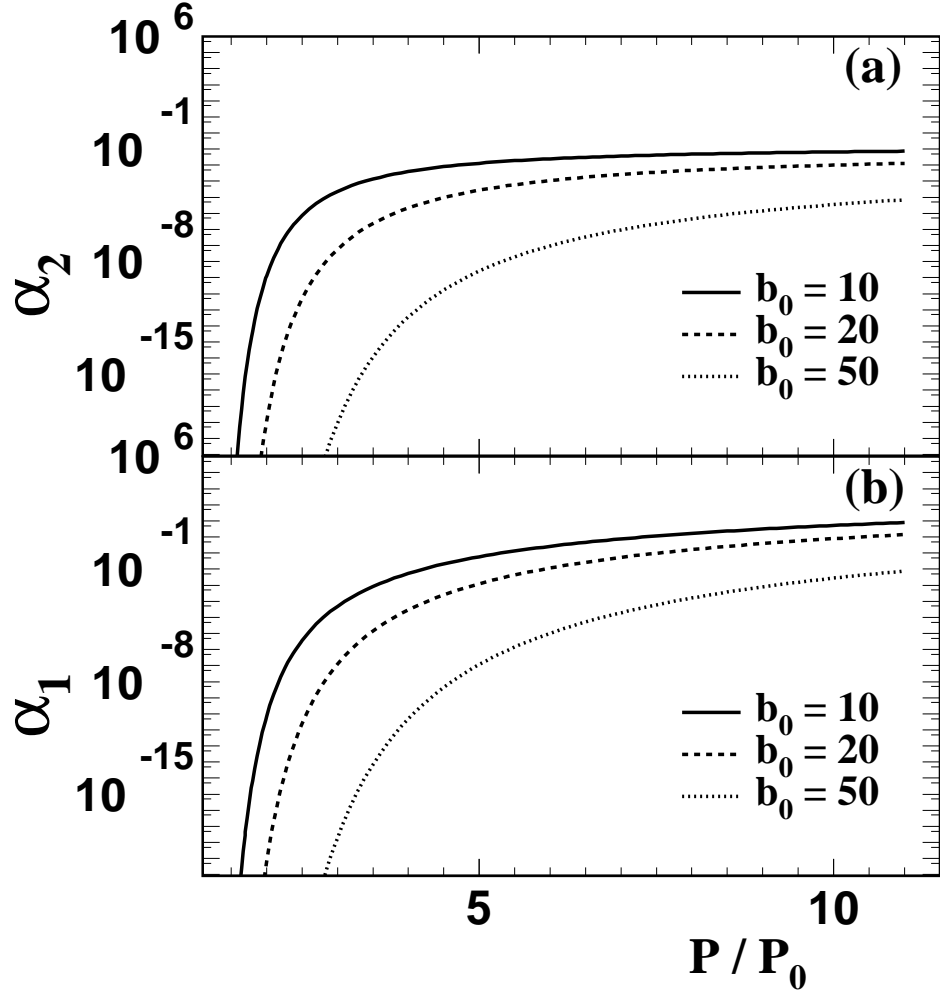


FIG. 1. Factors α_1 and α_2 as functions of the degree of vapour supersaturation p/p_0 calculated with $b_0 = 10$ (solid lines), 20 (dashed lines), and 50 (dotted lines).

TABLES

TABLE I. Power-law approximation of thermodynamic quantities near the critical point

Quantity	Power-law approx. at $T \rightarrow T_c$	critical exponent
σ	$\sigma_0 \theta^{2\nu}$	$\nu = 0.625$
Δn	$(\Delta n_0) \theta^\beta$	$\beta = 0.5$
λ	$\lambda_0 \theta^{\nu-\gamma}$	$\gamma = 1.0$
l	$l_0 \theta^\beta$	
ξ	$\xi_0 \theta^{-\nu}$	
$\Delta\mu$	$\propto \theta^\gamma$	